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(54) Title: RIGID POLYURETHANE FOAMS WITH IMPROVED PROPERTIES

(57) Abstract: In the process of the present invention, an organic polyisocyanate is reacted with a sorbitol-based polyether polyol having a number average molecular weight of from about 400 to about 1500, in the presence of a pentafluoropropane blowing agent, and a catalyst.

RIGID POLYURETHANE FOAMS WITH IMPROVED PROPERTIES

BACKGROUND OF THE INVENTION

The present invention relates to a process for the production of rigid polyurethane foams having improved demold and outstanding insulation properties.

5

Processes for the production of rigid polyurethane foams are known. Sucrose-based polyols are of particular interest as the primary isocyanate-reactive reactant because of their relatively low cost, high functionality and because they are relatively simple to produce. Processes for producing such sucrose-based polyols are disclosed, for example, in U.S. patents 3,085,085; 3,153,002; 3,222,357; 4,430,490; and 5,539,006. Each of these patents teaches that sucrose-based polyols are useful in the production of polyurethane foams.

15

At the present time, a major concern of foam producers, particularly rigid foam producers, is the development of rigid foam systems in which the chlorofluorocarbon blowing agent is replaced with a more environmentally acceptable blowing agent. HCFCs (i.e., hydrogen containing chlorofluorocarbons), HFCs (hydrogen containing fluorocarbons), and hydrocarbons such as n-pentane cyclopentane, isopentane and blends of these blowing agents are presently considered to be possible alternatives.

20

Dishart et al's paper entitled "The DuPont Program on Fluorocarbon Alternative Blowing Agents for Polyurethane Foams", Polyurethanes World Congress 1987, pages 59-66 discusses the investigation of various HCFCs as possible blowing agents for rigid polyurethane foams.

25

Various references have described the use of pentafluoropropanes as blowing agents in producing polyurethane foams. See, e.g., U.S. patents 5,496,866; 5,496,867; 5,426,127; 5,461,084; and 5,889,066.

5 Finally, several references have broadly suggested the use of sorbitol-based polyethers in producing polyurethane foams. See, e.g., U.S. patents 4,943,597; 5,798,533; 6,207,725; 6,284,812; 6,306,920; 6,339,110; 6,346,205; 6,380,275; and 6,433,032; and an article published in 2001 by Colvin, entitled "New Blowing Agents for Insulated Panels." Of
10 these references, U.S. patents 6,284,812; 6,306,920; and 6,380,275 and the Colvin article broadly suggest that sorbitol-based polyethers may be used with HFC-245fa.

15 A process in which for preparing a rigid foam having good physical properties, particularly good demold and insulating properties would, therefore, be advantageous. More particularly, it would be advantageous to produce a rigid foam from a pentafluoropropane blowing agent having lower freeze stable density at a lower overpack and improved k-factor and with other physical properties being at least equivalent to foams produced
20 from sucrose-based polyethers.

DESCRIPTION OF THE INVENTION

25 The present invention is directed to a process for the production of rigid polyurethane foams having excellent demold and insulation properties and to the foams produced by this process.

30 In the process of the present invention, an organic polyisocyanate is reacted with a sorbitol-based polyether polyol having a number average molecular weight of from about 400 to about 1500, in the presence of a pentafluoropropane blowing agent, and a catalyst. The foams produced according to the present invention exhibit lower K-factors, lower densities, lower mold lid opening values at freeze stable densities and comparable

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compressive strength (even though the core density is lower), when compared to foams produced from equivalent sucrose-based polyether polyols.

- 5 The sorbitol-based polyether is preferably an ethylene oxide, propylene oxide polyether having a number average molecular weight of from about 400 to about 1500, an ethylene oxide content of from about 10 to about 50% by weight, preferably from about 20 to about 40% by weight and a propylene oxide content of from about 50 to about 90% by weight,
10 preferably from about 60 to about 80% by weight, with the %s by weight being based on the total amount of ethylene oxide and propylene oxide used.

- The blowing agent is preferably a pentafluoropentane selected from
15 the group consisting of 1,1,2,2,3-pentafluoropropane (HFC-245ca), 1,1,2,3,3- pentafluoropropane (HFC-245ea), 1,1,1,2,3-pentafluoropentane (HFC-245eb) and 1,1,1,3,3-pentafluoropropane (HFC-245fa), with 1,1,1,3,3-pentafluoropropane being most preferred. The blowing agent is generally used in an amount of from about 5 to about 20% by weight (and
20 preferably from about 8 to about 16% by weight) based on the total weight of the foam formulation.

- The polyol and isocyanate are reacted at an isocyanate index of from about 0.9 to about 3.1, preferably from about 1.05 to about 1.55. The
25 foams of the invention generally have K-factors which are lower than the K-factors of the foams produced from equivalent sucrose-based polyether polyols. Typically, the foams produced herein will have K-factors of less than 0.140 Btu-in./hr.ft²°F measured at 75°F. The preferred foams of the invention will have K-factors of less than 0.135 and, in some instances,
30 even less than 0.130. If a K-factor of less than 0.130 is not required, it could still be advantageous to use a sorbitol-based polyol and use a lower amount of blowing agent to reduce cost.

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Any organic polyisocyanate may be used in the process of the present invention. Suitable isocyanates include aromatic, aliphatic, and cycloaliphatic polyisocyanates and combinations thereof. Examples of useful isocyanates include: diisocyanates such as m-phenylene diisocyanate, p-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 1,6-hexamethylene diisocyanate, 1,4-hexamethylene diisocyanate, 1,4-cyclohexane diisocyanate, hexahydrotoluene diisocyanate and its isomers, 1,5-naphthylene diisocyanate, 1-methyl-phenyl-2,4-phenyl diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate and 3,3'-dimethyl-diphenyl-propane-4,4'-diisocyanate; triisocyanates such as 2,4,6-toluene triisocyanate; and polyisocyanates such as 4,4'-dimethyl-diphenylmethane-2,2', 5,5'-tetraisocyanate and the polymethylene polyphenylpolyisocyanates.

Undistilled or a crude polyisocyanate may also be used in making polyurethanes by the process of the present invention. The crude toluene diisocyanate obtained by phosgenating a mixture of toluene diamines and the crude diphenylmethane diisocyanate obtained by phosgenating crude diphenylmethanediamine are examples of suitable crude polyisocyanates.

Preferred polyisocyanates for the production of rigid polyurethanes are methylene-bridged polyphenyl polyisocyanates and prepolymers of methylene-bridged polyphenyl polyisocyanates having an average functionality of from about 1.8 to about 3.5 (preferably from about 2.0 to about 3.1) isocyanate moieties per molecule and an NCO content of from about 28 to about 34% by weight, due to their ability to cross-link the polyurethane.

The polyisocyanate is generally used in an amount such that the isocyanate index (i.e., the ratio of equivalents of isocyanate groups to

equivalents of isocyanate-reactive groups) is from about 0.9 to about 3.0, preferably from about 1.0 to about 1.5.

The polyols employed in the process of the present invention are
5 polyether polyols prepared by reacting sorbitol and optionally other
initiators (with or without water) with ethylene oxide and/or propylene oxide
in the presence of an alkaline catalyst. The product is then treated with an
acid, preferably a hydroxy-carboxylic acid so as to neutralize the alkaline
catalyst. U.S. Pat. No. 4,430,490 (which discloses a suitable process for
10 such neutralization) is incorporated herein by reference. The acid used to
neutralize the alkaline catalyst present in the polyether polyol may be any
acid which will result in an acidified polyether polyol having a pH of from
about 4.0 to about 8.0, preferably from 5.5 to 7.5. Hydroxycarboxylic acids
are the preferred neutralizing acids. The total amount of alkylene oxide
15 used is selected so that the resultant polyol will have a number average
molecular weight of from about 400 to about 1500, preferably from about
600 to about 1200.

It is most preferred that the sorbitol-based polyether contain both
20 ethylene oxide and propylene oxide residues. In this case, it is preferred
that the sorbitol first be reacted with ethylene oxide and then propylene
oxide. The ethylene oxide is generally used in an amount of from about 10
to about 50%, preferably from about 20 to about 40% by weight of the total
alkylene oxide used. The propylene oxide is generally used in an amount
25 of from about 50 to about 90% by weight, and preferably from about 60 to
about 80% by weight of the total alkylene oxide employed,

Other polyols (e.g., i) polyether polyols which are based on
hydroxy-functional initiators other than sorbitol or are based on organic
30 polyamines and ii) polyester polyols) known to be useful in the production
of rigid polyurethane foams may, optionally, be used in combination with
the required sorbitol-based polyether polyol. When used, these optional

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polyols are present in an amount which is no greater than 90%, preferably from about 10 to about 85% and most preferably from about 25 to about 80% by weight of the total amount of polyol used (i.e., the total amount of sorbitol-based polyol and optional polyols).

5

Water may optionally be included in the reaction mixtures of the present invention. When used, the water is generally present in an amount of from about 0.2% to about 2.0%, and preferably from about 0.4 to about 1.5% by weight based on the total foam formulation.

10

Any of the catalysts known to be useful in the production of rigid polyurethane foams may be employed in the process of the present invention. Tertiary amine catalysts are particularly preferred. Specific examples of suitable catalysts include: pentamethyldiethylenetriamine, N-N-dimethylcyclohexylamine, N,N',N''-dimethylamino-propylhexahydrotriazine, and tetramethylethylenediamine. Pentamethyl-diethylenetriamine and N,N',N''-dimethylamino-propylhexahydrotriazine are particularly preferred. Organometallic catalysts (such as organotin compounds) of the type known in the urethane art can also be used.

20

Other materials which may optionally be included in the foam-forming mixtures of the present invention include: chain extenders, crosslinking agents, surfactants, pigments and/or colorants, fillers, antioxidants, flame retardants, and stabilizers.

25

Having thus described our invention, the following examples are given as being illustrative thereof. All parts and percentages given in these examples are parts by weight and percentages by weight, unless otherwise indicated.

EXAMPLES

The materials used in the following examples were as follows:

- 5 POLYOL A: a sucrose-based polyether polyol having an hydroxyl
 number of about 470, prepared by first reacting a
 sucrose/propylene glycol/water slurry with ethylene
 oxide and then propylene oxide in the presence of
10 KOH catalyst such that ethylene oxide comprised
 about 30% and propylene oxide comprised about 70%
 of the total alkylene oxide used. The polyol was then
 neutralized with lactic acid and distilled to remove the
 residual water.
- 15 POLYOL B: a sorbitol-based polyether polyol having an hydroxyl
 number of about 470, prepared by first reacting
 sorbitol with ethylene oxide and then propylene oxide
 in the presence of KOH catalyst such that ethylene
20 oxide comprised about 30% and propylene oxide
 comprised about 70% of the total alkylene oxide used.
 The polyol was then neutralized with lactic acid and
 distilled to remove the residual water.
- 25 POLYOL C: an aromatic amine-initiated polyether polyol having an
 OH number of 395 and an average OH functionality of
 about 4, commercially available from Bayer
 Corporation as Multtranol 8114.
- 30 POLYOL D: an aromatic polyester polyol having an OH number of
 240, commercially available from Stepan Company
 under the name Stepanol PS 2502a.

- 5 Mondur 1515: modified polymeric methylenediphenyl diisocyanate
 having an NCO content of about 30.5, commercially
 available from Bayer Corporation under the name
 Mondur 1515.
- DC-5357: a silicon surfactant available from Air Products and
 Chemicals, Inc. under the name Dabco DC-5537.
- 10 PDT: pentamethyldiethylenetriamine
- TPT: 1,3,5-tris(3-(dimethylamino)propyl)hexahydro - s -
 triazine

15 The foams were prepared by reacting the components listed in the
 following table in the amounts listed by mixing the polyols, catalysts,
 surfactant, water and blowing agent (HFC-245fa) to form a masterbatch.
 The masterbatch and isocyanate were then mixed using a Hennecke high-
 pressure foam machine equipped with an MQ 12-2 mixhead. The liquid
 output was maintained at a constant 60 lbs./min. and the recycle and pour
20 pressures were held at 1500 psig. The minimum fill density was
 determined from foam panels poured into a temperature controlled Brett
 mold at 120°F (49°C) with an internal volume of 79 inches (200 cm) by
 8 inches (20 cm) by 2 inches (5 cm).

25 Panels were then prepared at four higher densities at 0.10, 0.15,
 0.20 and 0.25 lb./ft³ over the minimum fill density. The lid opening of the
 Brett mold was determined on each of these panels. The top half of each
 panel was cut into ten sections of about 4 inches (10 cm) and subjected to
 -4 °F (-20°C) for at least 16 hours. The panel with the lowest density,
30 which exhibited no significant dimensional change, was considered to be
 freeze stable. Additional panels for foam properties were all prepared at
 this "freeze stable density" ("FSD" in the following table).

The K-factor was determined using a LaserComp 300 k-Factor instrument with 8 x 8 x 1 inch core foam samples. A mean temperature of 75°F was used.

- 5 The formulations tested and the results obtained were as indicated in the table.

Table

	Control	Example 1
POLYOL A	14.00	-
POLYOL C	38.50	38.50
POLYOL D	17.51	17.51
POLYOL B	-	14.00
PDT	2.83	2.83
TPT	1.06	1.06
Polycat-41	0.53	0.53
WATER	0.90	0.90
HFC 245fa	24.67	24.67
Total	100	100
Mondur 1515	98.2	98.2
Min. Fill (pcf)	1.88	1.88
FSD (pcf)	2.08	2.02
% Overpack	10.60%	7.40%
3 Minute Demold Lid Opening at FSD (in)	0.086	0.068
Fox k-factor 8" Fox K/ Molded Density 75°F Average	0.130 ± 0.001	0.128 ± 0.001
Compressive Strength (Psi)		
Perpendicular	21.2 ± 0.5 (5)	21.5 ± 0.4 (3)
Parallel	34.2 ± 0.7 (5)	33.1 ± 0.5 (3)
Compressive Strength (Psi)		
Perpendicular	21.2 ± 0.5	21.5 ± 0.4
Parallel	34.2 ± 0.7	33.1 ± 0.5
Core Density (pcf)	1.89 ± 0.02	1.81 ± 0.01

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the
5 invention except as it may be limited by the claims.

WHAT IS CLAIMED IS:

1. A process for preparing a rigid polyurethane foam comprising reacting:
 - a) an organic polyisocyanate with
 - 5 b) a sorbitol-based polyether polyol having a number average molecular weight of from about 400 to about 1500, in the presence of
 - c) a pentafluoropropane blowing agent, and
 - d) a catalyst.
- 10 2. The process of Claim 1, wherein said blowing agent is selected from the group consisting of 1,1,2,2,3-pentafluoropropane, 1,1,2,3,3-pentafluoropropane, 1,1,1,2,3-pentafluoropentane and 1,1,1,3,3-pentafluoropropane.
- 15 3. The process of Claim 2, wherein said sorbitol-based polyether polyol is an ethylene oxide, propylene oxide polyether polyol.
4. The process of Claim 2, wherein polyols which are not based on
20 sorbitol are also included in the reaction mixture.
5. The process of Claim 2, wherein water is also included in the reaction mixture.
- 25 6. A process for preparing a rigid polyurethane foam comprising reacting:
 - a) an organic polyisocyanate with
 - b) a sorbitol-based polyether polyol having a number average molecular weight of from about 400 to about 1500,
 - 30 b1) an o-toluene diamine-based polyether polyol,
 - b2) a polyester polyol, and
 - b3) water in the presence of

- c) a pentafluoropropane blowing agent, selected from the group consisting of 1,1,2,2,3-pentafluoropropane, 1,1,2,3,3-pentafluoropropane, 1,1,1,2,3-pentafluoropentane and 1,1,1,3,3-pentafluoropropane,
- 5 d) a tertiary amine catalyst.

7. The process of Claim 6, wherein said sorbitol-based polyether polyol is an ethylene oxide, propylene oxide polyether polyol.

INTERNATIONAL SEARCH REPORT

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US2004/000796

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G18/48 C08J9/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 306 920 B1 (HEINEMANN ET AL) 23 October 2001 (2001-10-23) column 1, line 60 - column 3, line 61; claims 1,3,5,8,12; example 5	1-5
X	US 6 086 784 A (BARTHELEMY ET AL) 11 July 2000 (2000-07-11) column 2, line 11 - line 52 claims 1,2; example 16	1-7
A	PATENT ABSTRACTS OF JAPAN vol. 0182, no. 68 (C-1202), 23 May 1994 (1994-05-23) & JP 6 041268 A (ACHILLES CORP), 15 February 1994 (1994-02-15) abstract ----- -/--	1-7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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